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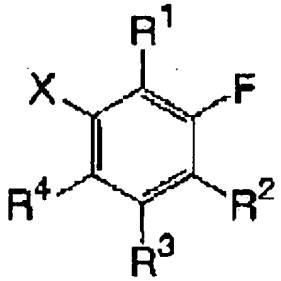
(54) META-FLUOROBENZENESULFONIC ACID DERIVATIVE AND DOPANT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a compound useful as a dopant giving a π-conjugated high-molecular compound with high electrical conductivity and also having the high electrical conductivity to even at high temperatures and humidities.

SOLUTION: This compound is a m-fluorobenzenesulfonic acid derivative of general formula [1] (where, X is sulfonic acid bearing a countercation; one of R1 to R4 is a carboxamido group, the other three being each H, F or an alkyl) to be used as the dopant.



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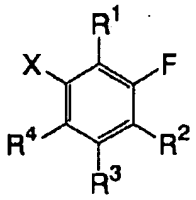
* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

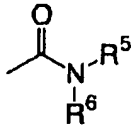
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the dopant agent of new m-fluorobenzene sulfonic-acid derivative and the conductive polymer matter which comes to reach.
[0002]
[Background of the Invention] In recent years, a new electronics ingredient is developed with development of electronics. Even if remarkable technological innovation progresses especially in the field of a functional organic material and it restricts to a conductive ingredient, there is also an example which the conductive polymer which doped the electronic receptiveness compound as a dopant is developed by electronic conjugated-system high polymers, such as polyacethylene, poly para-phenylene, polypyrrole, and the poly aniline, for example, has already been put in practical use as a capacitor electrode material, a cell electrode material, an antistatic ingredient, etc.
[0003] However, in order to expand the practicality of these conductive polymer matter, while aiming at further improvement in electrical conductivity, environmental stability, such as thermal resistance and moisture resistance, has been big technical problems.
[0004] this invention person is especially indicating that pi conjugated-system high molecular compound using m-sulfo benzamides as a dopant agent is the ingredient which combines high conductivity and high thermal resistance in JP,2000-204074,A about environmental stability to the technical problem towards these utilization.
[0005] That is, in the polypyrrole doped by m-sulfo benzamide, even when it holds in 150-degree C air, the fall of electrical conductivity is very loose, and it has found out continuing maintaining high conductivity 100S [/cm] or more. To be regretted, when moisture lives together in addition to high temperature, there is a trouble that conductivity falls in the polypyrrole doped by m-sulfo benzamide. Therefore, it can be said that the improvement in stability under the conditions, i.e., high humidity, with which moisture coexists under an elevated temperature is indispensable to practicality expansion of a conductive polymer.
[0006]
[Problem(s) to be Solved by the Invention] This invention aims at offer of the new compound for it to pi conjugated-system high molecular compound for the purpose of offer of the dopant material which can maintain high conductivity under an elevated temperature and a high humidity environment with high conductivity.
[0007]
[Means for Solving the Problem] In this invention, m-fluorobenzene sulfonic-acid derivative characterized by what is expressed with the following general formula [1] is offered.
[Formula 3]



...[1]

[1] The inside of a formula and X are sulfonic groups which have an opposite cation, are a carboxamide radical as which one of R1-R4 is expressed in the following general formula [2], and are [Formula 4].



...[2]

Other three may be mutually the same, or you may differ, and a hydrogen atom, a fluorine atom, or a with a carbon number of 20 or less alkyl group is expressed, and among [2] types, R5 and R6 may be mutually the same, or they may differ from each other, and express a hydrogen atom, a with a carbon number of 20 or less alkyl group, or a phenyl group.

[0008] said general formula [1] -- setting -- the opposite cation of a sulfonic group -- the [hydrogen ion, alkali-metal ion, alkaline-earth-metal ion, and periodic table] -- it is the desirable mode of this invention that it is the ion chosen from the group which consists of a VIII group's transition-metals ion.

[0009] Moreover, in said general formula [1], it is the desirable mode of this invention that it is the ion chosen from the group which the opposite cation of a sulfonic group becomes from a hydrogen ion, sodium ion, potassium ion, and iron (III) ion.

[0010] Moreover, in said general formula [1], it is the desirable mode of this invention that it is a hydrogen atom except [all] the carboxamide radical expressed with a general formula [2] among R1-R4.

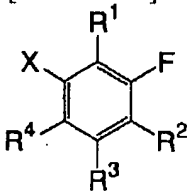
[0011] Moreover, in said general formula [2], it is the desirable mode of this invention that at least one of R5 and R6 is a hydrogen atom.

[0012] Furthermore, in this invention, the dopant agent of the conductive polymer matter characterized by consisting of the aforementioned m-fluorobenzene sulfonic-acid derivative is offered.

[0013]

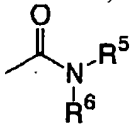
[Embodiment of the Invention] m-fluorobenzene sulfonic-acid derivative concerning this invention is expressed with the following general formula [1].

[Formula 5]



...[1]

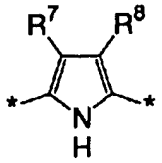
[1] It is the carboxamide radical as which X is a sulfonic group which has an opposite cation among a formula, and one of R1-R4 is expressed in the following general formula [2], and is [Formula 6].



...[2]

Other three may be mutually the same, or you may differ, and a hydrogen atom, a fluorine atom, or a with a carbon number of 20 or less alkyl group is expressed, and among [2] types, R5 and R6 may be mutually the same, or they may differ from each other, and express a hydrogen atom, a with a carbon number of 20 or less alkyl group, or a phenyl group.

[0014] If m-fluorobenzene sulfonic-acid derivative expressed with said general formula [1] is illustrated concretely A 4-fluoro-2-sulfo benzamide, a 5-fluoro-3-sulfo benzamide, A 4-fluoro-2-sulfo-N-hexyl benzamide, 4-fluoro-2-sulfo benzamide Sodium salt, Tris-(4-fluoro-2-sulfo benzamide) iron (III) complex salt, 4, the 5-difluoro-2-sulfo benzamides 4 and 5, a 6-trifluoro-2-sulfo benzamide, a 4-fluoro-2-sulfo-N-dodecyl benzamide, a 4-fluoro-2-sulfo benzanilide, etc. can be mentioned.
[0015] here -- the opposite cation of a sulfonic group -- the [hydrogen ion, alkali-metal ion, alkaline-earth-metal ion, and periodic table] -- it is desirable that it is the ion chosen from the group which consists of a VIII group's transition-metals ion. It is desirable that it is the ion chosen from the group which the opposite cation of a sulfonic group becomes from a hydrogen ion, sodium ion, potassium ion, and iron (III) ion especially. In the below-mentioned electrolytic oxidation polymerization method, this is for obtaining a suitable rate of polymerization by maintaining pH at a neutral region, and sodium ion and potassium ion are especially desirable. Moreover, in order to use oxidation and reduction of transition metals by the below-mentioned chemistry oxidation-polymerization method, especially iron (III) ion is desirable as a metal ion kind which can oxidize a pyrrole etc. easily.
[0016] Moreover, in said general formula [1], it is desirable that it is a hydrogen atom except [all] the carboxamide radical expressed with a general formula [2] among R1-R4 in respect of conductivity and thermal resistance here. Furthermore, in said general formula [2], it is desirable that at least one of R5 and R6 is a hydrogen atom conductivity and in respect of thermal resistance.
[0017] Especially the manufacture approach of m-fluorobenzene sulfonic-acid derivative expressed with a general formula [1] can be manufactured according to the synthetic roots, such as an approach of contacting it to suitable sulfonation agents, such as a sulfuric-acid, oleum, sulfur-trioxide, and sulfur-trioxide-pyridine complex and amidosulfuric acid, using as a raw material the precursor compound which does not have a sulfonic group, and, for example, sulfonating it, although not limited.
[0018] Especially a reaction condition is not limited on the occasion of the synthetic reaction using the aforementioned sulfonation reaction. For example, the ratio of the reaction of the m-fluorobenzene sulfonic-acid derivative precursor and the sulfonation agent which constitute a raw material is usually performed in 1:1-1:200 (mole ratio). Moreover, although a reaction solvent is not necessarily needed, when using it, a dichloroethane, a carbon tetrachloride, dioxane, etc. can be mentioned that what is necessary is just the thing which dissolves m-fluorobenzene sulfonic-acid derivative precursor and the sulfonation agent which are a raw material and by which the solvent itself is not sulfonated.
[0019] A moderate reaction rate is shown, advance of the side reaction by rapid generation of heat is avoided, and if reaction temperature is temperature which the sulfonation object which is m-fluorobenzene sulfonic-acid derivative precursor and the product which are a raw material further does not decompose, it will not be limited especially but will usually be performed at 0-150 degrees C. m-fluorobenzene sulfonic-acid derivative is compoundable with high yield such by adopting a reaction condition. Obtained m-fluorobenzene sulfonic-acid derivative can identify structure with a nuclear-magnetic-resonance spectrum and a mass analysis spectrum.
[0020] m-fluorobenzene sulfonic-acid derivative in connection with this invention is useful as a dopant agent doped to an electronic conjugated-system high polymer, and the conductive polymer which continues at a long period of time and discovers conductivity is given. If it is the high molecular compound which has the molecular structure of electronic conjugated system as an electronic conjugated-system high polymer, all can be used, and the conjugated-system macromolecule which repeated at least one of the pyrrole system specifically expressed with the following general formula [3], the thiophene system expressed with a general formula [4], and the aniline systems expressed with a general formula [5], and was constituted as a unit can be mentioned.
[0021]
[Formula 7]

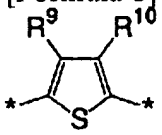


...[3]

Among an upper type, R7 and R8 may be mutually the same, or they may differ from each other, and are the alkyl group or alkoxy group of the shape of a hydrogen atom or a straight chain of the carbon atomic numbers 1-20, annular, and the letter of branching. Moreover, * shows the joint location of a repeat unit (the same is said of [4] types and [5] types).

[0022]

[Formula 8]

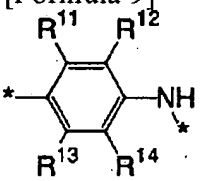


...[4]

Among an upper type, R9 and R10 may be mutually the same, or they may differ from each other, and are the alkyl group or alkoxy group of the shape of a hydrogen atom or a straight chain of the carbon atomic numbers 1-20, annular, and the letter of branching.

[0023]

[Formula 9]



...[5]

Among an upper type, R11, R12, R13, and R14 may be mutually the same, or may differ from each other, and are the alkyl group or alkoxy group of the shape of a hydrogen atom or a straight chain of the carbon atomic numbers 1-20, annular, and the letter of branching.

[0024] Use of the conjugation high molecular compound which repeats any one of the above-mentioned general formula [3], [4], and [the 5], and is constituted as a unit as an electronic conjugated-system high polymer is desirable, and use of the conjugation macromolecule of the polypyrrole system which repeats a general formula [3] and is especially constituted as a unit is desirable.

[0025] As an approach of doping m-fluorobenzene sulfonic-acid derivative to an electronic conjugated-system polymeric material, approaches generally used, such as an approach immersed in the solution of this derivative, the approach of using and carrying out the electrolytic oxidation polymerization of this derivative to a supporting electrolyte, and the approach of carrying out a chemistry oxidation polymerization using the transition-metals salt of this derivative, can be used.

[0026] In doping by dip coating, if it is a solvent with solvent power as a solvent at the time of dissolving m-fluorobenzene sulfonic-acid derivative, all can be used, for example, water, an acetonitrile, a nitrobenzene, propylene carbonate, ethylene glycol, etc. can be used.

[0027] In an electrolytic oxidation polymerization method, it is doped by impressing a predetermined current or potential to the solution which consists of an m-fluorobenzene sulfonic-acid derivative as a supporting electrolyte, and a monomer which can constitute the repeat unit of said high polymer. As a monomer which can constitute a repeat unit, pyrrole, thiophene, aniline, trans-1, 2-JI (2-thienyl) ethylene, trans-1, 2-JI (2-thienyl) butadiene, 3, and 4-ethylene dioxythiophene etc. is mentioned, for example.

[0028] Water, dimethyl formamide, an acetonitrile, propylene carbonate, ethylene glycol, a nitrobenzene, etc. are mentioned that what is necessary is just what dissolves the monomer which dissolves m-fluorobenzene sulfonic-acid derivative and can constitute a repeat unit as a solvent used for

an electrolytic oxidation polymerization reaction. an electrolytic oxidation polymerization -- usually -- a -100-150-degree C temperature requirement -- it can carry out preferably in a 0-50-degree C temperature requirement, and you may be which approach of chronopotentiometry and chronoamperometry. Moreover, as for an electrolytic oxidation polymerization, it is desirable to carry out under inert gas ambient atmospheres, such as nitrogen and an argon.

[0029] Doping is performed with a polymerization by doping by the chemistry oxidation-polymerization method by contacting in a solvent the transition metal complex which makes a ligand the conjugate base of m-fluorobenzene sulfonic-acid derivative, and the monomer used as the repeat unit which forms the high molecular compound which has the molecular structure of electronic conjugated system. As a central metal which constitutes a transition metal complex, iron, cobalt, a ruthenium, etc. can be mentioned, for example and iron is desirable also especially in these. A transition metal complex is usually used in the amount of 1-100 mols to one mol of monomers.

[0030] As a monomer which can constitute a repeat unit, pyrrole, thiophene, aniline, trans-1, 2-JI (2-thienyl) ethylene, trans-1, 2-JI (2-thienyl) butadiene, 3, and 4-ethylene dioxythiophene etc. can be used like the above. The solvent used at a reaction can mention water, dimethyl formamide, an acetonitrile, a tetrahydrofuran, propylene carbonate, ethylene glycol, etc. that what is necessary is just what dissolves the above-mentioned transition metal complex and a monomer. Polymerization temperature has desirable 0-50 degrees C, and 1 - 48 hours of reaction time are desirable. Moreover, as for a polymerization, it is desirable to be carried out under inert gas ambient atmospheres, such as nitrogen and an argon.

[0031] Thus, since high conductivity is maintainable under an elevated temperature and a high humidity environment with high conductivity, the electronic conjugated-system high polymer which doped m-fluorobenzene sulfonic-acid derivative of this invention obtained can be used suitable for a solid electrolytic capacitor, an antistatic film, an electromagnetic shielding material, electroconductive glue, a conductive paint, a wiring material, the electrode material for rechargeable batteries, a display ingredient, an overcurrent-protection component, a semiconductor device, etc.

[0032]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these examples at all.

[0033] (Example 1) After adding 4-fluoro benzamide 25g slowly at a room temperature, having added 65ml (sulfur-trioxide 30wt% excess property) of oleums to the 200ml three-lot flask, and stirring an oleum, stirring was continued at 70 degrees C for 13 hours, and 1 evening reaction mixture was left after that. Next, reaction mixture was supplied in 50g of ice, and the unreacted oleum was hydrolyzed. This reaction mixture was left and the depositing white powder was carried out the ** exception with the glass filter. the obtained white solid-state -- acetone 200ml -- it supplied to inside and stirring washing was performed. The vacuum drying was performed for the solid content obtained by carrying out this a ** exception under the room temperature for 24 hours, and 4-fluoro-2-sulfo benzamide 22.9g was obtained.

[0034] The obtained compound was identified by FD-mass spectrum (m/z=219) and 1 H-NMR. The analysis result was as follows.

1 H-NMR (DMSO-d6) analysis result delta(ppm) 7.20 (1H, d) 7.86 (1H, d) 8.21(1H, s) [0035] (Example 2) 4-fluoro-2-sulfo benzamide 21.9g compounded like the example 1 was dissolved in 200ml of pure water in the 500ml beaker. The sodium carbonate was added to this and pH of a water solution was adjusted to 7. After carrying out reduced pressure removal of the water by the evaporator, the vacuum drying was carried out for two days, and 23.4g of 2-carbamoyl-5-fluorobenzene sulfonic-acid sodium salt was obtained.

[0036] (Example 3) 61g of iron nitrate (III) 9 hydrates was put into 200ml beaker, and it dissolved in 100ml of pure water. Aqueous ammonia was added to this 15%, and pH of a water solution was set to 12. At this time, iron(III) hydroxide generated and the brown solid-state was obtained. this brown solid-state -- Kiriyama -- after filtering with the funnel (No.5B) and repeating rinsing 3 times, it dried under 1 evening vacuum.

[0037] The water solution which dissolved 4-fluoro-2-sulfo benzamide 21.9g compounded like the example 1 in 500ml of pure water was prepared, the iron-hydroxide whole quantity obtained by this was added, and it stirred for 6 hours. After carrying out insoluble matter in a water solution a ** exception, evaporation of the filtrate was carried out and the solvent was distilled off. Furthermore, one evening dried under the vacuum and 13.3g of tris-(2-carbamoyl-5-fluorobenzene sulfonyl) iron(III) salt was obtained.

[0038] (Example 4) 4-fluoro-2-sulfo benzamide 4.38g and pyrrole 1.34g obtained in the example 1 were dissolved in 200ml of pure water, and the reaction solution for electrolytic oxidation polymerizations was prepared. After it carried out bubbling of the nitrogen gas to this solution for about 15 minutes and it carried out the nitrogen purge to it, it was immersed at intervals of 1cm, and two SUTERENSU (sus304) plates of 4cm around were made into the operation pole and the counter electrode.

[0039] It energized for 40 minutes by constant current (1.25 mA/cm2) using the immersed SUTERENSU electrode of two sheets, and the electrolytic oxidation polymerization was performed. After pure water and an acetone washed the polypyrrole film generated on the electrode, it exfoliated from the electrode and was dried in the vacuum for 12 hours. It was 162 S/cm as a result of measuring the electrical conductivity of the obtained film with a four point probe method.

[0040] After holding the generated polypyrrole film in air and under a 150-degree C elevated temperature for 6 hours, as a result of measuring electrical conductivity with a four point probe method, it was 117S/cm.

[0041] On the other hand, the polypyrrole film obtained by the polymerization was immersed into pure water, and temperature of pure water was made into 90 degrees C, and was held for 12 hours. Subsequently, as a result of measuring electrical conductivity with a four point probe method after it took out the polypyrrole film out of pure water and it carried out the vacuum drying, it was 96S/cm.

[0042] (Example 5) 4.82g of 2-carbamoyl-5-fluorobenzene sulfonic-acid sodium salt and pyrrole 1.34g obtained in the example 2 were dissolved in 200ml of pure water, and the reaction solution for electrolytic oxidation polymerizations was prepared. After it carried out bubbling of the nitrogen gas to this solution for about 15 minutes and it carried out the nitrogen purge to it, it was immersed at intervals of 1cm, and two SUTERENSU (sus304) plates of 4cm around were made into the operation pole and the counter electrode.

[0043] It energized for 40 minutes by constant current (1.25 mA/cm2) using the immersed SUTERENSU electrode of two sheets, and the electrolytic oxidation polymerization was performed. After pure water and an acetone washed the polypyrrole film generated on the electrode, it exfoliated from the electrode and was dried in the vacuum for 12 hours. It was 103 S/cm as a result of measuring the electrical conductivity of the obtained film with a four point probe method.

[0044] After holding the generated polypyrrole film in air and under a 150-degree C elevated temperature for 7.5 hours, as a result of measuring electrical conductivity with a four point probe method, it was 100S/cm.

[0045] On the other hand, the polypyrrole film obtained by the polymerization was immersed into pure water, and temperature of pure water was made into 90 degrees C, and was held for 7.5 hours. Subsequently, as a result of measuring electrical conductivity with a four point probe method after it took out the polypyrrole film out of pure water and it carried out the vacuum drying, it was 102S/cm.

[0046] (Example 6) 1.3g of tris-(2-carbamoyl-5-fluorobenzene sulfonyl) iron(III) salt obtained in the example 3 was dissolved in 50ml of pure water in 50ml glassware. Pyrrole 0.13g was added to this water solution, and stirring was started. Several seconds after adding the pyrrole, a black solid-state began to deposit. the black solid-state after continuing one more evening of stirring -- Kiriyama -- a funnel (No.5A) -- come out -- another -- the bottom. After washing the obtained solid-state by acetone 10ml, one evening dried under the vacuum and 30mg of polymers was obtained.

[0047] 10mg of obtained polypyrrole polymers was taught to the tablet molding machine for infrared-spectrum sample molding, it was too heavy, and 200kg [/cm] when processed for 5 minutes, the disc-like plate with a diameter [of 1cm] and a thickness of 200 micrometers was able to be obtained. It was 36 S/cm as a result of measuring the electrical conductivity of the obtained disc-like plate with a four

point probe method.
[0048] After holding a disc-like polypyrrole plate in air and under a 150-degree C elevated temperature for 7.5 hours, as a result of measuring electrical conductivity with a four point probe method, it was 12S/cm.
[0049] On the other hand, the disc-like polypyrrole plate was immersed into pure water, and temperature of pure water was made into 90 degrees C, and was held for 7.5 hours. Subsequently, as a result of measuring electrical conductivity with a four point probe method after it took out the polypyrrole plate of PO discoid out of pure water and it carried out the vacuum drying, it was 30S/cm.
[0050]
[Effect of the Invention] New m-fluorobenzene sulfonic-acid derivative concerning this invention can be used as a doping agent of the conductive polymer matter. The conductive polymer which doped this compound and was obtained turns into an ingredient which has high conductivity, high thermal resistance, and high hot water resistance. Therefore, the obtained conductive polymer can be used as a capacitor electrode material, a cell electrode material, etc.

[Translation done.]